Doublet→quartet and doublet→doublet electronic transitions in NO_2 by electron impact[a)]

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The electron-impact energy-loss spectrum of nitrogen dioxide (NO_2) has been measured at impact energies of 25, 50, and 75 eV, and scattering angles varying from 5° to 80°. A previously unreported spin-forbidden doublet→quartet transition was observed at 4.49 eV, in excellent agreement with theoretical calculations. Doublet→doublet transitions were observed at 2.95, 5.81, 7.48, 8.64, 9.69, 10.52, 10.68, 10.94, and 11.20 eV, in agreement with previous experimental and theoretical work. In addition, numerous doublet→doublet transitions to superexcited states were observed.

INTRODUCTION

The electronic structure of NO_2 has been the subject of extensive experimental[1-14] and theoretical investigations.[15-26] Agreement between calculated and experimental doublet→doublet excitation energies has been quite good; however, prior to the present investigation, no experimental confirmation of calculated doublet→quartet transition energies was available. In order to further elucidate the electronic structure of NO_2 with particular emphasis on the low lying quartet states, we have applied the technique of low-energy variable-angle electron-impact spectroscopy to this molecule.

Electron impact spectroscopy has been shown to be a very powerful tool for the investigation of both spin and symmetry forbidden transitions.[27-30] The shape of the differential cross section (DCS) vs scattering angle curve is a sensitive indicator of the forbiddenness or allowedness of a transition. Optically allowed processes have very sharply forward peaked DCS's for impact energies 15 eV or more above the excitation threshold. In contrast, spin forbidden transitions (ones in which the spin quantum number changes by unity) have a nearly isotropic DCS over the angular range 10°–80°. Such transitions occur by the mechanism of electron exchange.[31] Consequently, the ratio of the intensity of a spin forbidden transition to that of a fully allowed transition increases by one to two orders of magnitude as the scattering angle increases from 10° to 80°.

The configuration of the $\tilde{X}\,^2A$ ground state of NO_2 is

$$(1a_1)^2(1b_2)^2(2a_1)^2(3a_1)^2(2b_2)^2(4a_1)^2(5a_1)^2(3b_2)^2(1b_1)^2(4b_2)^2(1a_2)^2(6a_1)^1 \text{ (Ref. 26)}.$$

Transitions may occur to either valence or Rydberg-like orbitals. Single valence or Rydberg excitations from the $6a_1$ orbital may only result in doublet excited states. In addition, valence transitions from lower lying orbitals to the $6a_1$ may also only result in doublet excited states. All other transitions will result in both doublet and quartet excited states. The excitations to valence excited states are of particular interest in this study since, because of orbital overlap considerations, the doublet–quartet splittings are expected to be larger than those for Rydberg excitations, leading to easier resolution of quartet states from doublet states.

EXPERIMENTAL

The electron spectrometer used in this study was that described by Kuppermann *et al.*[27] Spectra of NO_2 in the energy loss range 0→20 eV were obtained at impact energies of 25, 50, and 75 eV and scattering angles from 5° to 80°. Sample pressures in the scattering chamber were typically 4 mTorr as indicated by an uncalibrated Schulz–Phelps ionization gauge while the incident electron beam current was approximately 80 nA. The energy resolution was electron optically set to 120 meV (FWHM). The NO_2 sample was obtained from Matheson Gas Products with a stated purity of 99.5% and was subjected to several freeze–pump–thaw cycles before use.

The equilibrium constant for the reaction $2NO_2 = N_2O_4$ may be calculated from the free energy data of Giauque and Kemp[32] to be 6.49 atm^{-1}. Therefore, N_2O_4 constitutes a less than 0.1% impurity at our operating pressure.

DISCUSSION

Figure 1 shows the electron impact spectrum of NO_2 from 1.6 to 9.6 eV energy loss at an impact energy of 50 eV and scattering angles of 10° and 80°. Relatively intense features appear in both spectra at 2.95, 5.81, 7.48, and 8.64 eV. No inelastic electronic features are observed below 1.6 eV. Two electric dipole allowed transitions, the $\tilde{X}^2A_1 \rightarrow \tilde{A}\,^2B_1$ and the $\tilde{X}\,^2A_1 \rightarrow 1\,^2B_2$, are predicted to lie near 3 eV energy loss.[18-24,26] Krauss

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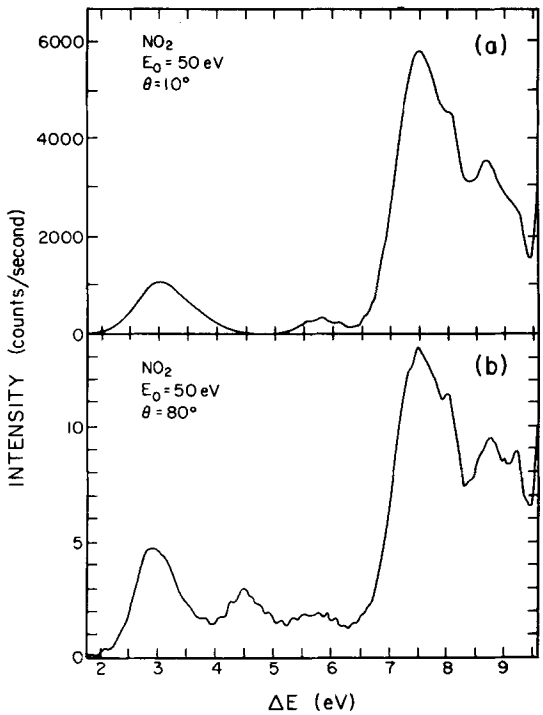

FIG. 1. Electron energy-loss spectrum of NO_2 at a scattering angle of (a) 10°, and (b) 80°; 50 eV impact energy; 8×10^{-8} A incident beam current; 5 mTorr sample pressure reading from an uncalibrated Shulz-Phelps gauge; resolution approximately 0.12 eV (FWHM).

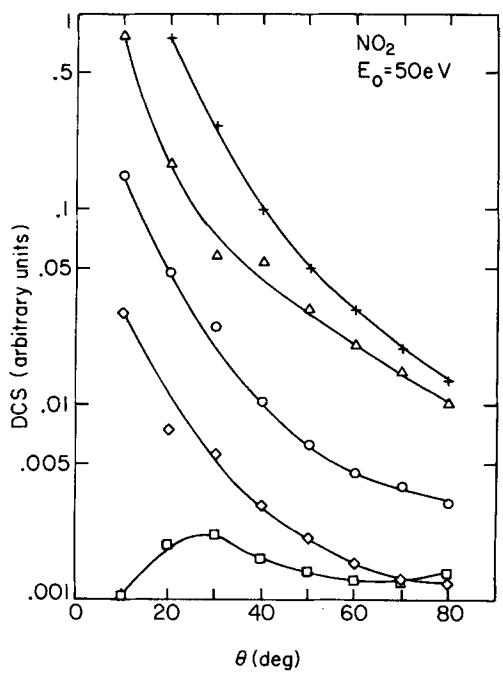

FIG. 2. Differential cross sections of NO_2 as a function of scattering angle at an incident electron energy of 50 eV; for elastic scattering (+) and for excited states: $D_{2.95}$ (○), $Q_{4.49}$(□), $D_{5.81}$ (◇), and $D_{7.48}$ (△). The elastic peak DCS was multiplied by 0.1 before plotting. The letters D and Q stand for doublet and quartet upper states, respectively, and the index represents the corresponding transition energy in eV.

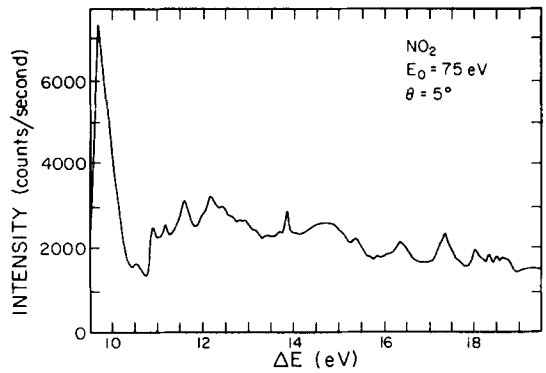

FIG. 3. Electron energy-loss spectrum of NO_2 at a scattering angle of 5°, 75 eV incident electron energy; 8×10^{-8} A incident beam current; 3 mTorr sample pressure measured by an uncalibrated Schulz–Phelps gauge.

et al.,[13] on the basis of a long vibrational progression observed in their 100 eV, 0° electron impact spectrum, have assigned the feature with an intensity maximum at about 2.96 eV in their spectrum to the $\tilde{X}^2A_1 - 1^2B_2$ valence transition. Our observed transition energy of 2.95 eV is in excellent agreement with theirs and we assign this feature to that same transition.

A transition with an intensity maximum at about 2167 Å (5.72 eV) has been observed in the optical spectrum of Nakayama *et al.*[5] In our spectra, a feature is observed with an intensity maximum at 5.81 eV in very good agreement with the results of Nakayama *et al.*[5] This transition has been tentatively identified as the $\tilde{X}^2A_1 - \tilde{C}$ transition by Herzberg[9] (no symmetry designation has been given); however, it has been suggested that the progression observed between 2000 and 2350 Å (6.18 – 5.28 eV) may be part of the $\tilde{X}^2A_1 - \tilde{B}^2B_2$ system.[9] The CI calculations of Shih *et al.*[23] indicate only one transition in the 5.5 to 6 eV range, the $\tilde{X}^2A_1 - \tilde{B}^2B_2$ at 5.51 eV. Additional optical studies by Coon *et al.*[11] have indicated a transition with an intensity maximum at 5.22 eV which has been assigned to the $\tilde{X}^2A_1 - \tilde{B}^2B_2$. Shih *et al.*[23] have suggested that the true vertical excitation energy may be higher than that of the most probable vibrational transition. In addition, previous electron impact studies[10] have observed only one transition in this region, at about 5.7 eV. It is therefore not clear from our results whether the 5.81 eV feature may be assigned as the $\tilde{X}^2A_1 - \tilde{B}^2B_2$ or whether the $\tilde{X} - \tilde{B}$ transition, which is quite weak (the absorption coefficient is roughly 20% of that of the $\tilde{X} - \tilde{C}$ transition[5]), is simply not resolved from an $\tilde{X}^2A_1 - \tilde{C}$ transition of unknown symmetry.

The transition which we observe with an intensity maximum at 7.48 eV has been reported previously as a broad maximum between 1750 and 1600 Å (7.1 and 7.75 eV) in the optical work of Nakayama *et al.*[5] and as an intense peak at 7.5 eV in the electron impact results of Edqvist *et al.*[10] This feature has been assigned as the $\tilde{X}^2A_1 - \tilde{D}^2A_1$ transition corresponding to the Rydberg excitation $6a_1 - 3s$. Shih *et al.*[23] have calculated an excitation energy of 7.71 eV for this transition in good agreement with experimental results.

TABLE I. Transition energies for NO_2.

State	Excitation	Theoretical (eV)	Previous experimental (eV)	This work (eV)
$\tilde{x}\,^2A_1$	Ground state	0	0	0
$\tilde{A}\,^2B_1$	$6a_1 \rightarrow 2b_1$	2.13,[a] 2.58,[b] 1.75,[d] 2.45[e] 2.8,[f] 2.46,[g] 2.79,[h] 2.93[i] 2.97[k]	2.7–3.26[n]	
$^2B_2$	$4b_2 \rightarrow 6a_1$	3.15,[c] 3.33,[d] 3.03[e] 3.4,[f] 2.43,[g] 3.22[h] 3.40,[i] 3.59[k]	2.96,[q] 3.0[e]	2.95
$^2A_2$	$1a_1 \rightarrow 6a_1$	2.46,[b] 1.68,[c] 4.13[d] 3.09,[e] 3.4,[f] 2.15[g] 3.25,[h] 3.61,[i] 3.63[k]		
$^4B_2$	$1a_2 \rightarrow 2b_1$	3.38,[d] 3.80,[e] 4.6[f] 2.88,[g] 4.04,[h] 4.85[i] 4.47,[j] 4.53[k]		4.49
$^4A_2$	$4b_2 \rightarrow 2b_1$	3.43,[d] 3.81,[e] 4.7[f] 3.10,[g] 4.09,[h] 4.72[i] 4.30,[j] 4.37[k]		
$^2A_2$	$4b_2 \rightarrow 2b_1$	4.82,[e] 5.04[f]		
$\tilde{B}\,^2B_2$	$1a_2 \rightarrow 2b_1$	3.95,[a] 3.73,[b] 5.18,[e] 5.51[h]	5.22[e] 5.72,[m] 5.7[o]	5.81
$^2A_2$	$4b_2 \rightarrow 2b_1$	6.5,[e] 6.76[h]		
$\tilde{D}\,^2A_1$	$6a_1 \rightarrow 3s$	7.0,[a] 9.87,[b] 7.71[h]	7.1 – 7.75,[m] 7.5[o]	7.48
$^2B_1$	$6a_1 \rightarrow 3p_y$	8.62[h]		
$^2A_1$	$6a_1 \rightarrow 3p_z$	8.73[h]	8.55,[l] 8.65,[m] 8.6[o]	8.64
$^2B_2$	$6a_1 \rightarrow 3p_x$	8.84[h]		
$^2B_2$	$1a_2 \rightarrow 2b_1$	9.07[h]		
$^4B_2$	$4b_2 \rightarrow 3s$	9.20[h]		
$^2B_2$	$6a_1,\ 4b_2 \rightarrow 2b_1^2$	9.33[h]		
$^4A_2$	$1a_2 \rightarrow 3s$	9.62[h]		
$^2B_2$	$4b_2 \rightarrow 3s$	9.70	9.66[o]	9.69
$^2A_2$	$1a_2 \rightarrow 3s$	9.86		
$^2A_1$	$4b_2 \rightarrow 3p_\sigma$		10.46[o]	10.52
$^2A_2$	$1a_2 \rightarrow 3s$	10.9		
$^2B_1$	$1a_2 \rightarrow 2p_\sigma$		10.85	10.94
$^2B_2$	$4b_2 \rightarrow 3s$		11.12	11.20
$^2B_2$	$4b_2 \rightarrow 4s$		11.55	11.61
$^2B_2$	$4b_2 \rightarrow 5s$		12.11	12.20
$^2B_2$	$4b_2 \rightarrow 6s$		12.40 14.7	12.46 14.62
$^2B_2$	$3b_2 \rightarrow 3s$		15.38	15.36
$^2A_2,\ ^2B_2$	$3b_2 \rightarrow 3p_\pi$		16.35	16.37
$^2A_1,\ ^2B_1$	$3b_2 \rightarrow 3d_\pi$		17.22	17.23
$^2B_2$	$3b_2 \rightarrow 4s$		17.34	17.35
$^2A_2,\ ^2B_2$	$3b_2 \rightarrow 4p_\pi$		17.63	17.69
$^2B_2$	$3b_2 \rightarrow 5s$		18.01	18.03
$^2B_2$	$3b_2 \rightarrow 6s$		18.32	18.33
$^2B_2$	$3b_2 \rightarrow 7s$		18.49	18.5
$^2B_2$	$4a_1 \rightarrow 3p_\sigma$		18.63	18.65

[a]Reference 15. [b]Reference 16. [c]Reference 17. [d]Reference 18. [e]Reference 19. [f]Reference 20. [g]Reference 22. [h]Reference 23. [i]Reference 24. [j]Reference 25. [k]Reference 26. [l]Reference 1. [m]Reference 5. [n]Reference 8. [o]Reference 10. [p]Reference 11. [q]Reference 13.

The transition which we observe with a maximum at 8.64 eV has been reported previously by Price and Simpson[1] at 1450 A (8.55 eV) and by Edqvist *et al.*[10] at 8.6 eV. This transition has been assigned as due to excitation from the $6a_1$ orbital to the $3p_{x,y,z}$ orbital. The calculated energies for excitation to the $3p_x$, $3p_y$, and $3p_z$ orbitals are 8.84, 8.62, and 8.73 eV, respectively,[23] and are in excellent agreement with the experimental work.

In addition to these previously reported doublet → doublet transitions, we observe a feature at 4.49 eV in the 80° spectrum which is not observed in the 10° spectrum and has not been reported previously. The DCS's for this feature and several other features are shown in Fig. 2. The method used for obtaining DCS curves has been described previously.[29] The DCS for the 4.49 eV feature is constant to within a factor of about 2 over the angular range 10°–80°. This behavior is exactly as is expected for a spin forbidden transition, so the feature may be definitively assigned as doublet → quartet in nature. Two doublet-to-quartet transitions have been theoretically predicted to lie in this region, the $\tilde{X}^2A_1 \rightarrow {}^4B_2(1a_2 \rightarrow 2b_1)$ and the $\tilde{X}^2A_1 \rightarrow {}^4A_2(4b_2 \rightarrow 2b_1)$.[18–20,22–26] Due to resolution limitations, we are unable to determine which of these transitions is the primary contributor to the 4.49 eV feature we observe.

Figure 3 shows the spectrum of NO_2 at an impact energy of 75 eV and a scattering angle of 5° in the energy loss region 9.5–19.5 eV. The excitation energies of the numerous transitions which appear in this spectrum are listed in Table I. Edqvist *et al.*,[10] also using the electron impact technique, have assigned the features in this energy loss region to various Rydberg series. Our results are in excellent agreement with those of Edqvist *et al.*[10] In addition to the features which may be correlated with previously identified transitions, we observe several weak transitions between 12.5 and 14 eV and between 15.5 and 16 eV energy loss, including one fairly intense feature at 13.86 eV which appears at excitation energies which exactly correspond to intense transitions of nitric oxide.[30] We therefore believe that these features are due to a small nitric oxide impurity.

In summary, we have used the technique of low-energy, variable angle, electron impact spectroscopy to investigate the excited states of NO_2. We have observed a previously unreported doublet → doublet transition at 4.49 eV. In addition, doublet → doublet transitions were observed at excitation energies which were in good agreement with previous experimental and theoretical work.

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